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# Experimental investigation of the effect of thermal hysteresis in $MnFeP_{1-x}As_x$ materials applied in an AMR device

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## ABSTRACT

The magnetocaloric material series $MnFeP_{1-x}As_x$, exhibiting a 1st order phase transition are possibly good candidates for magnetic refrigeration devices operating at room temperature (Brück *et al.*, 2005). These materials have intrinsic hysteresis (thermal and magnetic) and the impact of this on magnetic refrigeration devices has not yet been thoroughly investigated in the literature.
Here, the thermal hysteretic magnetocaloric properties are studied using vibrating sample magnetometry (VSM) and how this influences actual refrigeration performance, using an established active magnetic regenerator (AMR) test device (Bahl *et al.*, 2008) with a flat plate regenerator of a single Curie temperature ($T_C$) material.
We find that the maximum adiabatic entropy change does not depend on the thermal history of the material, but the peak temperature is shifted 1.5 K for fields up to 1.5 T when measured at a constant field during heating or cooling. There is possibly an increase of the entropy change peak width of 0.3 K when cooling compared to heating. These results are confirmed by experiments on an AMR test device.

## 1. INTRODUCTION

Magnetic refrigeration has the potential to become a viable environmentally friendly and efficient alternative to conventional vapor-compression refrigeration with the discovery of the giant magnetocaloric effect (Pecharsky and Gschneidner, 1997). Since then a lot of research has been put into finding the optimal material for low priced household refrigeration devices, working around room temperature. One candidate is the 1st order material $MnFeP_{1-x}As_x$. The magnetocaloric effect (MCE) is found to be comparable with other candidates working at room temperature (Tegus *et al.*, 2002). The Curie temperature can be tuned by changing the P/As ratio (Brück *et al.*, 2004), making it customizable for specific application needs and for multilayered magnetocaloric regenerators. Due to the nature of 1st order phase transitions, the magnetic phase transition is coupled to a structural transition, giving rise to the desired large MCE but also both magnetic and thermal hysteresis. Magnetic hysteresis causes a direct entropy loss in each AMR cycle, which in a worst case scenario can nullify the MCE entirely (Tocado *et al.*, 2006). Thermal hysteresis does not cause any direct AMR cycle losses, but it makes the magnetocaloric properties of the material dependent on the thermal history as will be shown. This is of great importance when designing a refrigeration device optimized for certain temperature conditions.
Here we investigate the thermal hysteresis of a $MnFeP_{1-x}As_x$ compound by VSM and measure how these properties influence the performance of an actual AMR test device.

## 2. EXPERIMENTS

The material used is provided by BASF as a part of a series of $MnFeP_{1-x}As_x$ compounds with varying Curie temperatures. In these experiments a single of these materials is investigated. The material is bulk sintered and then cut into plates.

### 2.1 Magnetization measurements

In order to measure the magnetic entropy change, the magnetization was measured as a function of applied magnetic field and temperature using the isofield method where temperature is varied point by point at constant applied magnetic field. Initiating the measurements at temperatures far from $T_C$ in each temperature

run avoids complications due to mixed ferro- and paramagnetic states, as described by (Caron *et al.*, 2009). These measurements were done on a commercial LakeShore 7407 VSM. The magnetization was measured under constant applied magnetic fields of 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 T, while the temperature range was 275 - 320K in steps of 1 K for both heating and cooling at each field. From these results the entropy change was calculated by employing the Maxwell relation

$$\Delta S = \int_0^H \left.\frac{\partial M}{\partial T}\right|_H dH. \tag{1}$$

The magnetization gradient for each field curve is numerically calculated for each temperature and then integrated over the different field values. The magnetization measurements and the corresponding calculated entropy changes are shown in Figure 1.

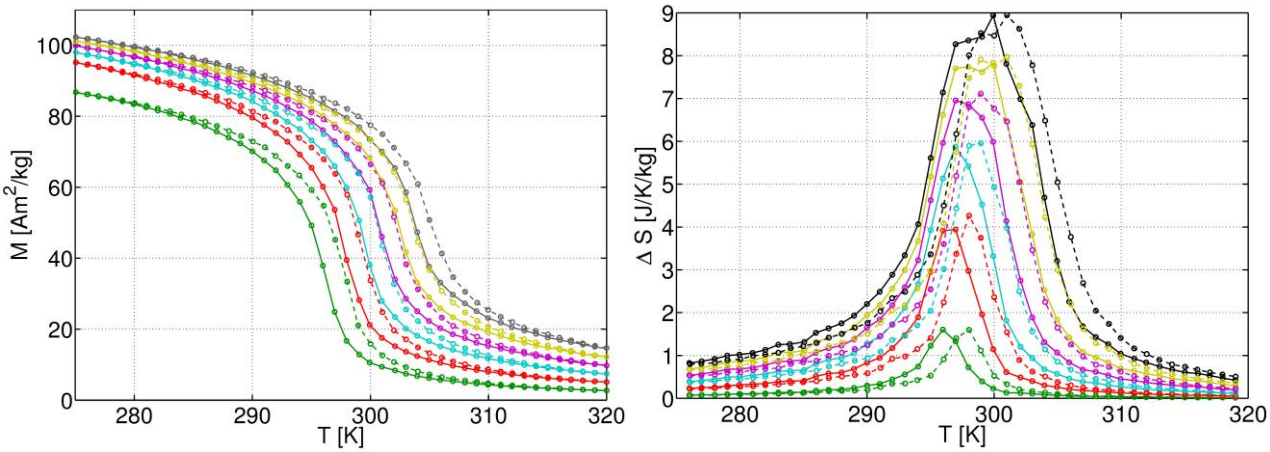


**Figure 1. Measured magnetization and integrated entropy change curves with applied magnetic fields of 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 T. The solid and dashed lines represent cooling and heating, respectively.**

Each entropy change curve fits well to a Lorentzian of the form

$$\Delta S = \frac{\Delta S_{\max}}{1 + \left(\frac{T - T_p}{w}\right)^2} \tag{2}$$

where $\Delta S_{\max}$ is the maximum entropy change, $T_p$ the transition peak temperature and $2w$ the full width at half maximum (FWHM).

In Figure 2 the transition peak temperature is shown as a function of applied field. A clear thermal hysteresis is seen. The transition temperature is shifted about 1.5 K depending on whether the sample is cooled or heated. The transition temperature increases linearly with about 2.4 K/T in both cases. However, it is noted that the linearity seems to deviate for fields below 0.5 T. This effect was also seen by (Zang *et al.*, 2010), where it is attributed to the effects of the demagnetizing field and domains beginning to be significant in these low applied fields.

Figure 3 shows $\Delta S_{\max}$ and the FWHM of the entropy change peak for a given field. $\Delta S_{\max}$ is seen to increase towards a saturation point, following a non-linear curve. Mean field theory predicts a power law with exponent 2/3 (Oesterreicher, 1983). It is reported that 2nd order materials do indeed follow a power law with an exponent close to 2/3 (Franco, 2006). However, this 1st order material does not fit very well to a power law; at least not in the measured field range.

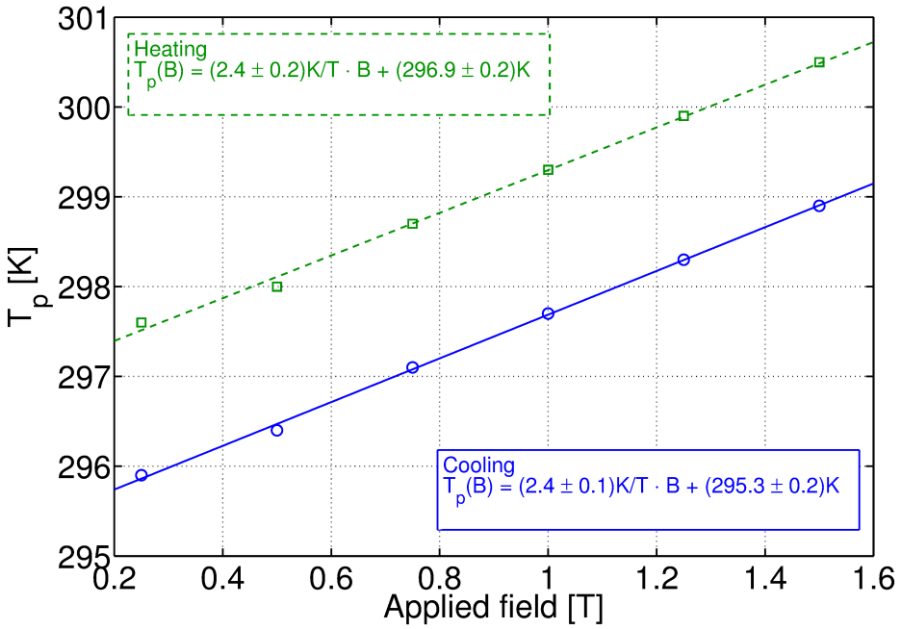


**Figure 2. The magnetic phase transition temperature as a function of applied field for both heating and cooling.**

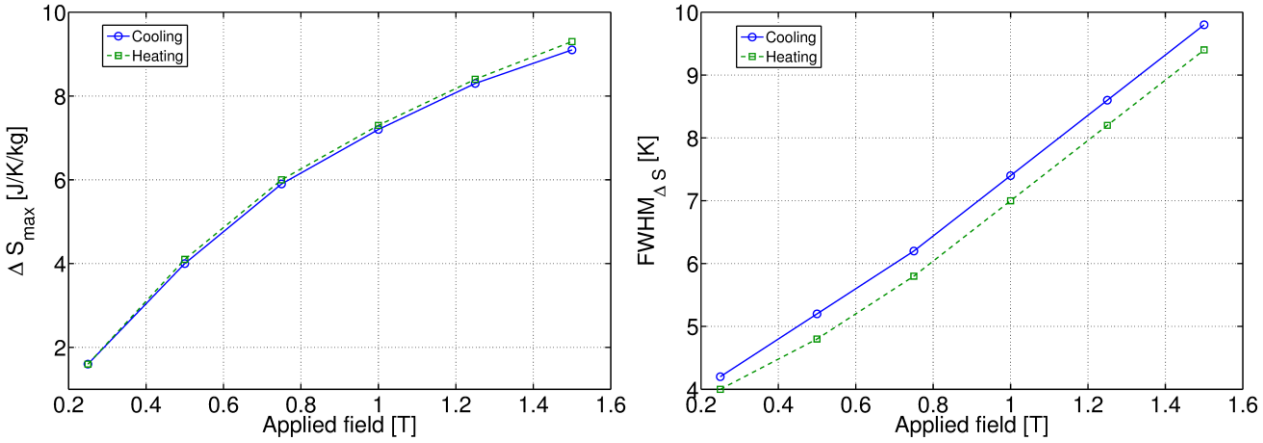


**Figure 3. The peak maximum and the full width at half maximum of the entropy change peaks as a function of applied field.**

The FWHM of the entropy change peak increases linearly with field, when the field is larger than 0.5 T. For both heating and cooling the FWHM increases about 4.5 K/T across the entire range of fields. There is possibly minor thermal hysteresis between heating and cooling, where cooling consistently gives a 0.3 K wider peak.

### 2.2 AMR test device

In order to test the actual performance of the material and investigate if any thermal hysteresis effects are present, the $MnFeP_{1-x}As_x$ material was used in larger quantities as refrigerant in an AMR device, described in (Bahl *et al.*, 2008).

The regenerator is shown in Figure 4. It consists of 12 stacked, flat plates; having length, width and thickness of 36 mm, 24 mm and 1 mm respectively. The plates are separated by 0.6 mm and have a total mass of 63 g. In cycles, the material is magnetized and demagnetized from 0 to 1 T by a permanent magnet, with an AMR frequency of about 0.2 Hz. The hot side of the regenerator is kept at constant temperature through a heat bath at a controlled temperature. The cycle is run until a steady temperature span across the regenerator is reached. This was done for a range of hot side temperatures between 314 - 294 K. The regenerator was then cooled to 278 K and then the measurements were redone from 294 - 314K.

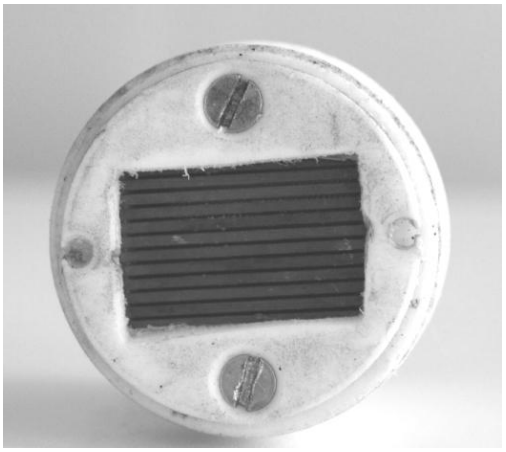

**Figure 4. The stacked flat plates of $MnFeP_{1-x}As_x$. The plates are 36 mm long (into the page), 24 mm wide and 1 mm thick. The plates have a separation of 0.6 mm.**

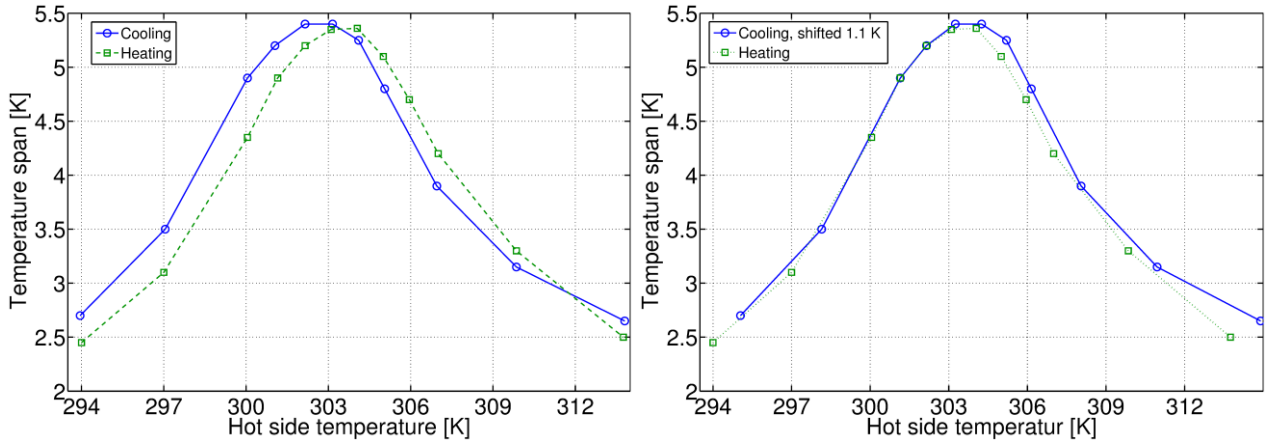


**Figure 5. A stack of 12 flat plates of $MnFeP_{1-x}As_x$, totaling 63 g, was used as a regenerator, cycling between 0 and 1 T magnetic field with a frequency of 0.2 Hz. (Left) The measured temperature span between the hot and cold side of the AMR device. (Right) Cooling curve shifted 1.1 K.**

Figure 5 shows the results of the AMR test device experiments. The maximum temperature span is just below 5.5 K for both experiments and the peak performance temperature is about 302.5 K and 303.5 K when cooling and heating, respectively. These temperatures are higher than what is measured by magnetometry, since the material is submitted to a temperature gradient across the regenerator. When the two curves are shifted about 1.1 K across the entire temperature range it is noticed that the width of the heating curve is a bit narrower when heating compared to cooling. This is a minor compression of the peak width, but it is consistent for all measured temperatures and with the VSM measurements.
When looking at the temperature span for the cooling curve at 314 K it seems higher than expected. However, this is the first measured point in the series of experiments. The regenerator was not heated up above 314 K prior to this measurement and the actual thermal history is unknown.
The AMR test device experiments have been repeated several times, and the result remains the same. The material seems to partially stay in the originating magnetic phase during the experiments, regardless of the hundreds of magnetization and demagnetization cycles during the recording of each measurement.

## 3. SUMMARY

Through VSM measurements it was found that the investigated $MnFeP_{1-x}As_x$ material experiences clear thermal hysteresis. There is a thermal shift in peak entropy change temperature of 1.5 K. A similar effect is also observed during the application of the material in a device performing AMR cycles, where the peak performance temperature is shifted 1.1 K. VSM measurements also implied that the FWHM of the entropy

change peak was 0.3 K wider when coming from the paramagnetic state, compared to originating in the ferromagnetic state. A similar broadening was also seen in the AMR experiments.

## ACKNOWLEDGEMENTS

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